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RECENT DEVELOPMENTS ON METALS AND ENERGY EXTRACTION FROM WASTE STREAMS

Characterization of Nickel in Chromite Beneficiation Tailings by Mineral Liberation Analysis and Its Recovery by H_2SO_4 Leaching Followed by Oxalic Acid Precipitation

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This study investigated the recovery of nickel from tailings (0.2% Ni) obtained in a chromite beneficiation plant using H_2SO_4 leaching followed by oxalic acid precipitation. The tailings were characterized using mineral liberation analysis. Ni was found as Fe-Ni, Fe-Ni-Co sulfide minerals, which were encapsulated in serpentine, olivine, pyroxene and clinochlore. Liberated fine chromite minerals benefited from magnetic separation followed by Falcon concentrator. A chromite product with a grade $> 37\%$ was obtained. The effect of leaching conditions including acid concentration, temperature, time and solid-to-liquid ratio on the leaching behavior of Ni was investigated based on the Taguchi approach. It was possible to extract Ni with a rate of $> 98\%$ from the tailings using the following conditions: H_2SO_4 concentration of 3 M, solid-to-liquid ratio of 1:20 and ambient temperature for 2 h. Finally, Ni was precipitated as an oxalate form with a precipitation rate of 72%. It is believed that implementing additional purification methods like solvent extraction may be essential to obtain a high-purity nickel product from the leach solution of oxalate precipitate. Experimental results indicate that the tailings used in this study are a good alternative as Ni resource in the near future.

INTRODUCTION

Nickel, with its superior properties, holds significant potential for numerous applications, including stainless steel, alloys, electronics and batteries. Moreover, it is classified as one of the most critical raw materials in reports published by the E. Commission[1] and USA Energy[2] because of its importance for clean energy applications, especially for Li-based battery production. The demand for Ni is expected to continue rising in the near future because of the rapid growth of the battery industry.[3,4] Ni is produced from sulfide and laterite ores by using various hydrometallurgical methods: high pressure acid leaching (HPAL),[5,6] atmospheric leaching (AL),[7] heap leaching (HL)[8,9] and bioleaching.[10] In these processes, inorganic acids (HCl,[11] H_2SO_4[12,13]), organic acids or their mixtures (ascorbic acid:H_2SO_4,[14] citric acid[15]) have been tested to determine the leaching mechanism for Ni extraction from different resources. Bioleaching has recently garnered significant attention and interest in various fields because it is an environmentally friendly and economically viable approach to metal extraction from complex sulfides.[16–19] It is anticipated to ultimately assume a crucial role as an alternative to conventional hydrometallurgical techniques, primarily because of its inherent cost-effectiveness in terms of both capital and operational expenditures. Kursunoglu et al.[20] conducted a study on the leaching methodology for Caldag lateritic nickel ore, employing the analytic hierarchy process (AHP) to weigh various operational criteria. These criteria encompassed essential factors such as leaching

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parameters (acid consumption, temperature, leaching time, pressure and particle size), extraction efficiency and economic considerations (initial investment and overall cost). The findings indicated that HPAL became a favorable choice when the primary economic criteria were prioritized. One of the key advantages of AL is however its cost-effectiveness, requiring lower capital and energy investments compared to HPAL. Despite this cost advantage, AL still manages to achieve comparable nickel and cobalt recoveries, making it a viable and efficient option in ore processing.

Recently, many studies have examined the leaching behavior of Ni from laterite ores under atmospheric conditions. Borda and Torres[21] conducted an in-depth investigation into laterite leaching by employing sodium citrate as an alternative reagent to traditional inorganic acids. Their study also delved into assessing the impact of both pyro- and hydrometallurgical pre-treatments on ore morphology and structure. The findings revealed that while citrate exhibited a preference for nickel in selectivity, its dissolution process remained closely linked to iron within the ore. Prameswara et al.[22] reported on their study involving the optimization of the atmospheric direct leaching process through the utilization of a Box-Behnken experimental design. The laterite ore utilized in the study was sourced from a mining site located in Morowali, Indonesia. The researchers found that the ZLT model aptly described and characterized this specific leaching process. Dong et al.[23] examined the influence of pre-roasting on the atmospheric sulfuric acid leaching behavior of saprolitic laterites sourced from Indonesia. It was found that the alteration of mineral structures induced by the roasting process played a pivotal role in determining metal extraction yields, with subsequent modifications to the specific surface area also contributing significantly. These findings hold significance for advancing the development of a more efficient atmospheric acid leaching process tailored for laterite ores. He et al.[24] conducted a study focused on improving the recovery of nickel from limonitic laterite. They initially utilized response surface methodology to optimize the parameters of the nitric acid pressure leaching process for limonitic laterite, aiming to determine the ideal conditions. Subsequently, they explored two enhancement strategies: bleed air treatment and the incorporation of a surfactant. The outcomes demonstrated that both bleed air treatment and the introduction of a surfactant were effective in enhancing the leaching of limonitic laterite. During leaching, some impurities such as Mg and Fe may dissolve alongside Ni from the ore. Partial neutralization is typically used to remove Fe^{3+} ions from the acid leach solution of laterite. However, during this process, significant amounts of Mg^{2+}, Ni^{2+}, Co^{2+} and $SO_2{}^{-4}$ are lost. With increasing initial Fe^{3+} concentration and solution pH, the severity of loss increases with the precipitation of Fe^{3+}. A high Fe^{3+} ion concentration in the solution caused a significant loss of Mg^{2+}, Ni^{2+} and Co^{2+} ions. In addition, with an increase in the solution pH, the loss of Mg^{2+}, Ni^{2+} and Co^{2+} ions increased.[25] Das and Le[26] conducted a study concentrating on goethite precipitation derived from a synthetically reduced AL solution through an oxidation method. Their primary objective was to investigate iron removal and the consequential nickel and cobalt losses from solutions rich in iron. The study affirmed the formation of goethite due to iron precipitation, likely occurring through intermediate phases of ferrihydrite and schwertmannite. Furthermore, the research demonstrated that the crystallinity of goethite increased with prolonged duration, elevated temperatures and higher initial Fe(II) concentrations in the feed. Importantly, the study emphasized the critical role of precise pH control in achieving efficient iron removal through goethite precipitation.

Cr-rich product obtained from processes involving laterite or other sources of chromium may find potential applications across various industries. The utilization of Cr-rich products largely depends on the composition, purity and specific properties of the product. For instance, integrating minute quantities of alloying elements into low alloy steel substantially bolsters its resistance to corrosion. Particularly, minor additions of chromium up to 5 wt.% exert a substantial influence in enhancing this property. Studies have emphasized that even a slight increase in chromium content within low alloy steels leads to an augmentation of chromium within the resulting corrosion products. Consequently, this augmentation reinforces the effectiveness of these products in providing robust protection against corrosion.[27] The saleable Cr_2O_3 grade in the chromite market is required to be at least 40%. Metallurgical, chemical or refractory-grade chromite concentrates can be recovered from low-grade chromite beneficiation plant tailings.[28,29]

Astuti et al.[30] recently focused on the recovery of nickel from a pregnant leached solution without the initial removal of impurities. Specifically, they employed oxalate precipitation as a direct method for nickel recovery. The resulting product, known as mixed oxalate precipitate, contained a variety of metals, with nickel constituting approximately 78% of the composition. This research highlighted the feasibility of employing a straightforward approach, involving atmospheric citric acid leaching and subsequent oxalate precipitation, as an alternative method for extracting nickel and other valuable metals from nickel laterite ores. Gulcan et al.[31] explored a chemical precipitation method to synthesize nickel oxalate. This approach was chosen because of its suitability for large-scale production, as it requires less equipment and entails lower energy consumption compared to alternative methods. Herein, it was aimed to investigate the recovery of Ni from chromite beneficiation tailings containing

0.2% Ni by using a hydrometallurgical approach. Although the Ni content in the tailings is too low to apply the beneficiation process based on the current Ni price, it is thought that the high demand for Ni for use in the production of Li-based batteries will make this process profitable. Therefore, mineral liberation analysis was carried out to determine the properties of the tailings including modal mineralogy, mineral associations, calculated assay and liberation degree. Prior to conducting H_2SO_4 leaching, gravity methods (magnetic separation and Falcon concentrator) were performed to obtain liberated chromite minerals. The effect of leaching temperature, acid concentration, reaction time and solid-to-liquid ratio on the extraction behavior of Ni and Cr in a H_2SO_4 solution was investigated based on the Taguchi approach. Finally, Ni was precipitated with the addition of oxalic acid.

MATERIALS AND METHOD

Materials

The tailings used in this study were provided by the Akmetal Company in Aladağ-Adana, Turkey. The chemical composition of the tailings determined by X-ray fluorescence (XRF, Panalytical MiniPal) was as follows: 16.30% Fe_2O_3, 32.42% MgO, 43.41% SiO_2, 3.01% Cr_2O_3, 1.01% CaO, 1.04% Al_2O_3 and 1.77% others with a loss on ignition value of 1.15%. The nickel content in the tailings was measured at 200 ppm through analysis with atomic absorption spectrometry (AAS) using a Perkin Elmer 900 H instrument and inductively coupled plasma optical emission spectroscopy (ICP-OES) utilizing a Perkin Elmer Optima 8300 device. Both instrumental analysis methods were performed for double checking. Sulfur content in the tailings varies between 0.001% and 0.002%. The chemicals employed, sulfuric acid (H_2SO_4, 95–97% purity, Merck) and sodium hydroxide (NaOH, $\geq$ 98% purity, Merck), were directly used without any additional purification. Distilled water was utilized in preparing the desired acid concentration.

Methods

The experimental procedure conducted in this study comprises different stages: (1) characterization, (2) magnetic separation followed by Falcon concentrator and (3) H_2SO_4 leaching and oxalic acid precipitation. Each of these stages is explained in detail below.

Mineral Liberation Analysis

Prior to performing the mineral liberation analysis, the sample was ground in a ball mill to reduce its particle size below 100 μm. After that, it was classified as the following size ranges: $-100 + 75$ μm, $-75 + 50$ μm and $-50 + 38$ μm. Afterwards, representative samples were prepared using a Quantachrome Mini rotary riffler. These samples were mixed with resin in the mold. In a follow-up, resin mounts were polished for mineral liberation analysis, which was carried out using FEI Quanta 400 scanning electron microscope, mineral liberation analysis Suite 3.1 software and Bruker Xflash 6030 Dual EDS detector. Modal mineralogy, mineral associations, calculated assay and liberation degree properties of the tailings were determined. Furthermore, the liberation degree of the sample was examined under the binocular microscope.

Physical Separation

In this stage, the recovery of chromite mineral fines from the tailings with a particle size of < 100 μm was investigated by using an Eriez brand L4-20 WHIMS model high-intensity electromagnetic wet separator, followed by a Falcon concentrator (Sepro-L40.R3.0 Lenze). The slurry was prepared at a solid-to-liquid ratio of 1:4 for wet magnetic separation, and the magnetic field was fixed at 1 T. The slurry was stirred at 300 rpm for 1 min prior to feeding into the magnetic separator. After the magnetic separation, the obtained magnetic and non-magnetic products were weighted and prepared for chemical analysis to determine their Cr_2O_3 and Ni contents. In a follow-up, the enrichment of Cr_2O_3 in the magnetic product was provided by a Falcon concentrator under the following conditions: solid-to-liquid ratio of 1:5, fluidization water of 4 lpm and centrifugal force of 150 G. Light and heavy products were obtained, and their Cr and Ni contents were determined by AAS and ICP-OES. The distribution of Ni in each product was determined, and the light product obtained in the Falcon concentrator was used to investigate the recovery of Ni in the subsequent section.

Acidic Leaching and Precipitation

The leaching tests were carried out in a 300-mL glass jacketed reactor equipped with a glass condenser that was used to minimize evaporation. The reaction temperature was provided by a circulation water bath. The slurry was mixed at a stirring speed of 300 rpm (MTOPS MS300HS). When the reaction time was over, the mixing of the slurry was stopped, the slurry was filtered using Whatman 1 filter paper, and the concentration of metal (Ni and Cr) in the leachate was analyzed by AAS and ICP-OES. The effects of acid concentration, reaction time, temperature and solid-to-liquid ratio on the extraction behaviors of Ni and Cr from the product were investigated based on the Taguchi approach (L16, 4^4). Through the Taguchi approach, the obtained results were converted into three categories of signal-to-noise (S/N) ratios: (1) larger to better, (2) smaller to better and (3) nominal to better. For the extraction of Ni, larger to better was selected, whereas the smaller to better was selected as the output parameter for the extraction of Cr. The four independent variables with four levels can be seen in Table I. The obtained results were examined using MINITAB 19 software.

After each leaching test, the extraction rates of the metals from the tailings were calculated by using the following Eq. 1.

$$X = \frac{C_t \times V_F}{W_0 \times H_0} \times 100 \qquad (1)$$

where X is the extraction rate of the metal, C_t is the Ni or Cr concentration in the leachate (mg/L), V_F is the volume of the analyzed leachate (L), H_0 is the metal concentration in the sample (mg/kg), and W_o is the weight of the used sample in the leaching test (kg).

The precipitation test of Ni from the pregnant leach solution (PLS) with a volume of 250 mL was carried out in a 500-mL beaker with the addition of oxalic acid (1 M, 250 mL, Sigma-Alrich, purity: ≥ 99%) at a temperature of 90°C for 3 h. The solution was stirred at a speed of 300 rpm. The pH of the solution was kept constant as 0.5 by adding NaOH. The precipitation rate of Ni was calculated based on the difference of the Ni concentration before and after the precipitation test according to the following Eq. 2.

$$P = \frac{C_1 \times V_1 - C_2 \times V_2}{C_1 \times V_1} \times 100 \qquad (2)$$

where P is the precipitation rate of the Ni (%), C_1 is the initial metal concentration in the leachate (mg/L), C_2 is the final metal concentration in the leachate (mg/L), V_1 is the initial volume of the leachate (L), and V_2 is the final volume of the leachate (L).

RESULTS AND DISCUSSION

Mineral Liberation Analysis of the Tailings

Some properties of ore or tailings including mineral liberation size, mineral associations, free surface, grain size, distribution of valuable metals and mineralogical occurrence are of highly important to determine their beneficiation methods.[19,20] These properties can be determined by mineral liberation analysis, which consists of a software package and scanning electron microscope (SEM) together with energy-dispersive spectrum (EDS) analyzer. In this study, the mineral liberation analysis was carried out on the tailings prepared in different particle sizes: (1) − 100 + 75 μm, (2) − 75 + 50 μm and (3) − 50 + 38 μm. It was understood from the modal mineralogical analysis that it was mainly composed of serpentine (82.33%), olivine (7.58%), pyroxene (2.98%), magnesite (2.61%), spinel chromite (2.13%) and other minerals (2.41%) including enstantite, quartz, Fe-oxide, dolomite, clinochlore, grossular, kaolinite, albite, actinolite, zoisite, K-feldspar, andradite and Al-oxide (Fig. 1), which is in close relationship to the findings of Wang et al.[32] The study findings indicate that chromite ore processing residue comprises various components, including Mg-Al spinel, chromite, calcium ferrite, chlorite and brownmillerite. Although

Table I. Experimental parameters used in the leaching test according to the Taguchi approach (L16, 4^4)

Experimental parameters
Acid concentration: 1 M, 3 M, 5 M and 7 M
Time: 0.5 h, 1 h, 2 h and 3 h
Temperature: 25°C, 45°C, 65°C and 85°C
Solid-to-liquid ratio of 1:5, 1:10, 1:15, 1:20

Experiment no.	Acid concentration	Time	Temperature	Solid-to-liquid ratio
No. 1	1	0.5	25	1:5
No. 2	1	1	45	1:10
No. 3	1	2	65	1:15
No. 4	1	3	85	1:20
No. 5	3	0.5	45	1:15
No. 6	3	1	25	1:20
No. 7	3	2	85	1:5
No. 8	3	3	65	1:10
No. 9	5	0.5	65	1:20
No. 10	5	1	85	1:15
No. 11	5	2	25	1:10
No. 12	5	3	45	1:5
No. 13	7	0.5	85	1:10
No. 14	7	1	65	1:5
No. 15	7	2	45	1:20
No. 16	7	3	25	1:15

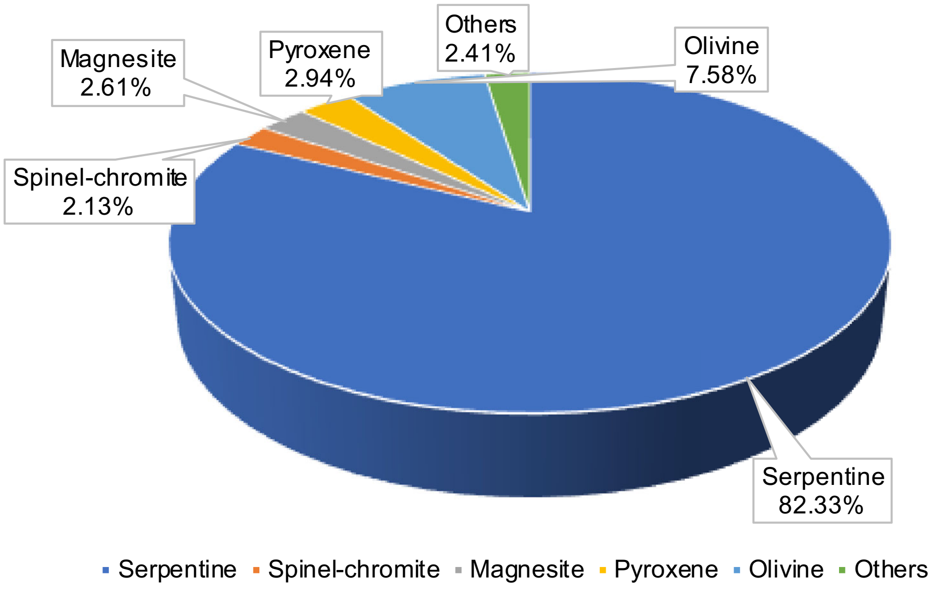

Fig. 1. Modal mineralogical composition of the tailings (wt.%, the value given here is the average value calculated from samples with a size of − 106 + 75, − 75 + 50 and − 50 + 38 μm).

previous research reports changes in their accounts of the origins and deposits of chromite, there is a common consensus that chromite minerals are typically associated with magmatic processes and are commonly found in ultrabasic rock formations.[33] In a recent study by Pownceby et al.,[34] a detailed characterization was carried out on chromite ore sourced from South Africa. The primary mineralogical components were found to be spinel phases, primarily ferrian-magnesiochromite and aluminum-chromite. Additionally, accessory phases included enstatite, hematite and plagioclase enriched in anorthite.

The backscattered electron images (BES) given in Fig. 2a, b, c and d show liberated chromite particles and their associations with other minerals (pyroxene and serpentine) in the tailings. It was determined that the free surface of spinel-chromite particles in the tailings was found to be 26.42% (− 106 + 75 μm), 25.78% (− 75 + 50 μm) and 55.21% (− 50 + 38 μm) (Fig. S1(a) (see online supplemental material)). The mineral textures displayed a coarse-grained assemblage featuring irregularly shaped, predominantly liberated spinel grains. Alongside these liberated spinel grains, there were composite particles comprising serpentine and pyroxene mineral phases. Figure S1(b) shows the liberation degree of the spinel-chromite mineral in the online supplementary material (ESM). Furthermore, optical microscope images given in the ESM (Fig. S2) indicated that many liberated chromite particles were observed, and their recovery may be possible using centrifugal gravity processes such as Falcon, Knelson or Multi-Gravity Separators. Therefore, it was decided to conduct the Falcon concentrator process after conducting the magnetic separation prior to conducting H_2SO_4 leaching.

It was possible to detect Ni-bearing minerals in the tailings by mineral liberation analysis. Backscattered SEM images indicated that Fe-Ni-Co sulfide and Fe-Ni were identified as nickel phase present in the tailings (Fig. 3). Moreover, the EDS spectra of those observed minerals in BSE images can be seen in the ESM (Fig. S3). Based on the BSE images, it was observed that the bright particle corresponds to nickel sulfide, consistent with the findings of Lim et al.[35] This observation was further validated by the mineral liberation analysis classified images. The images of mineral liberation analysis particles confirmed that a significant part of Ni-bearing minerals was detected in serpentine group mineral. Ni-bearing minerals encapsulated in other mineral phases such as serpentine, pyroxene, clinochlore and olivine. Fe-Ni and Fe-Ni-Co sulfide minerals were determined together. Table II summarizes the presence of Ni-bearing minerals in other mineral phases by mass.

Moreover, mineral liberation analysis confirmed that there was no Ni-bearing mineral identified as free mineral in the tailings (− 106 + 75 μm) and 93.64% of Fe-Ni mineral appeared to occur at binary with serpentine (91.69%) and olivine (1.95%) minerals (Table III).

Physical Separation Tests

Magnetic separation technique is widely used to improve the Cr:Fe ratio in Turkish magnesian-type chromite ores.[36,37] The recovery of fine chromite particles from the tailings was investigated by high-intensity magnetic separation and Falcon concentrator processes. It was possible to obtain the

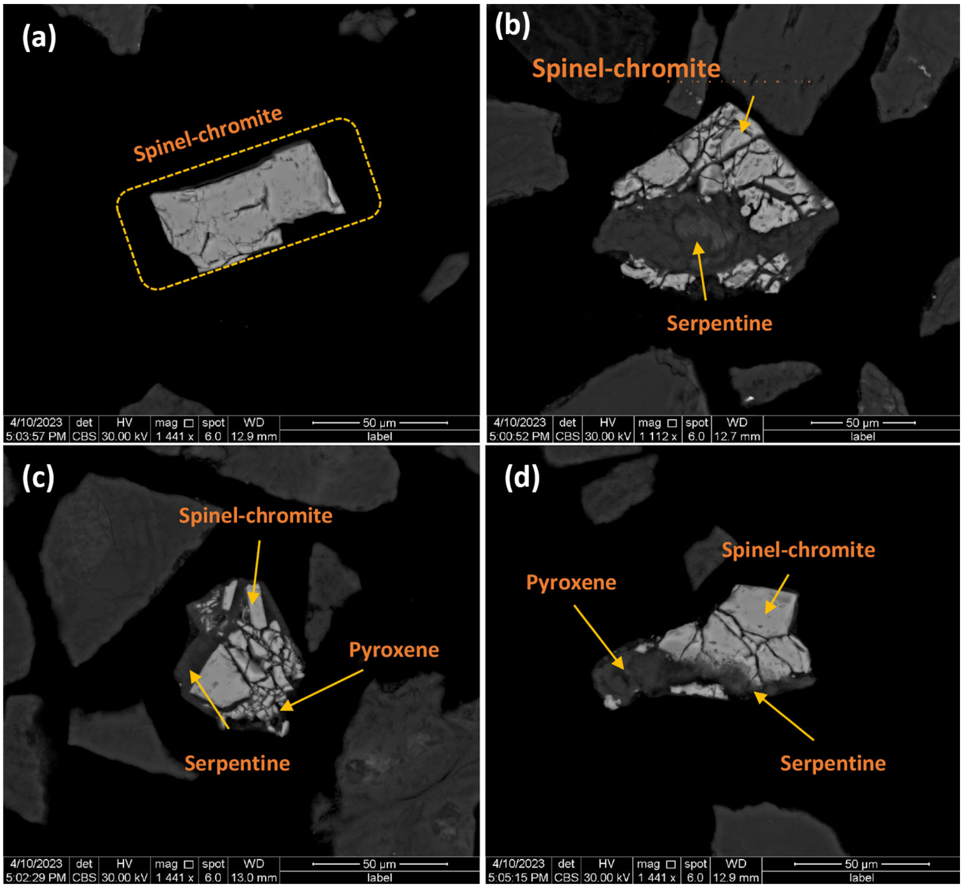

Fig. 2. Backscattered electron images and mineral liberation analysis classified images: (a) liberated, (b) binary, (c) and (d) ternary + particle spinel-chromite mineral.

magnetic product with a Cr_2O_3 content of 21.12%, and its recovery was 75.71% at a magnetic field strength of 1 T. However, the magnetic and non-magnetic products did not show any difference in terms of their Ni concentration, and their Ni contents were found to be around 200 ppm by AAS and ICP-OES for each product. Therefore, the non-magnetic product was used in the following leaching process because of its low Cr_2O_3 content. Moreover, the magnetic product was fed into the Falcon concentrator working at the aforementioned conditions, and the heavy product with a Cr_2O_3 content of 37.45% could be obtained. Rath et al.[38] used Falcon concentrator to obtain a concentrate with similar grade and recovery efficiency from the tailings of a chromium concentration plant in India. The experimental results obtained in this stage are listed in Table IV.

Acidic Leaching and Precipitation Tests

A series of the leaching experiments was carried out based on the Taguchi approach to determine the effect of leaching parameters including acid concentration, leaching time, leaching temperature and solid-to-liquid ratio on the extraction of Ni and Cr from the sample, which was obtained as the light product in the Falcon concentrator. The experimental results given in Table V show that the Ni extraction rate from the tailings was in a range of 6.55% and 98.88%, based on the leaching conditions, while the Cr extraction rate varied between 0.07% and 5.38%.

The primary leaching of the metals in H_2SO_4 solution can be written as follows:

$$NiS + H^+ = Ni^{2+} + H_2S \tag{3}$$

$$Ni_3S_2 + H^+ = 2NiS + Ni^{2+} + H_2 \tag{4}$$

$$NiS + 4H_2SO_{4(l)} = 4SO_{2(g)} + NiSO_{4(a)} + 4H_2O \tag{5}$$

$$CoS + 4H_2SO_{4(l)} = 4SO_{2(g)} + CoSO_{4(a)} + 4H_2O \tag{6}$$

$$FeS + 4H_2SO_{4(l)} = 4SO_{2(g)} + FeSO_{4(ia)} + 4H_2O \tag{7}$$

It was possible to dissolve Ni with an extraction rate of > 90% under different leaching conditions (for example, experiment nos. 4, 6 and 15). In these experiments, the solid-to-liquid ratio was 1:20. A decrease in the solid-to-liquid ratio (decreasing pulp

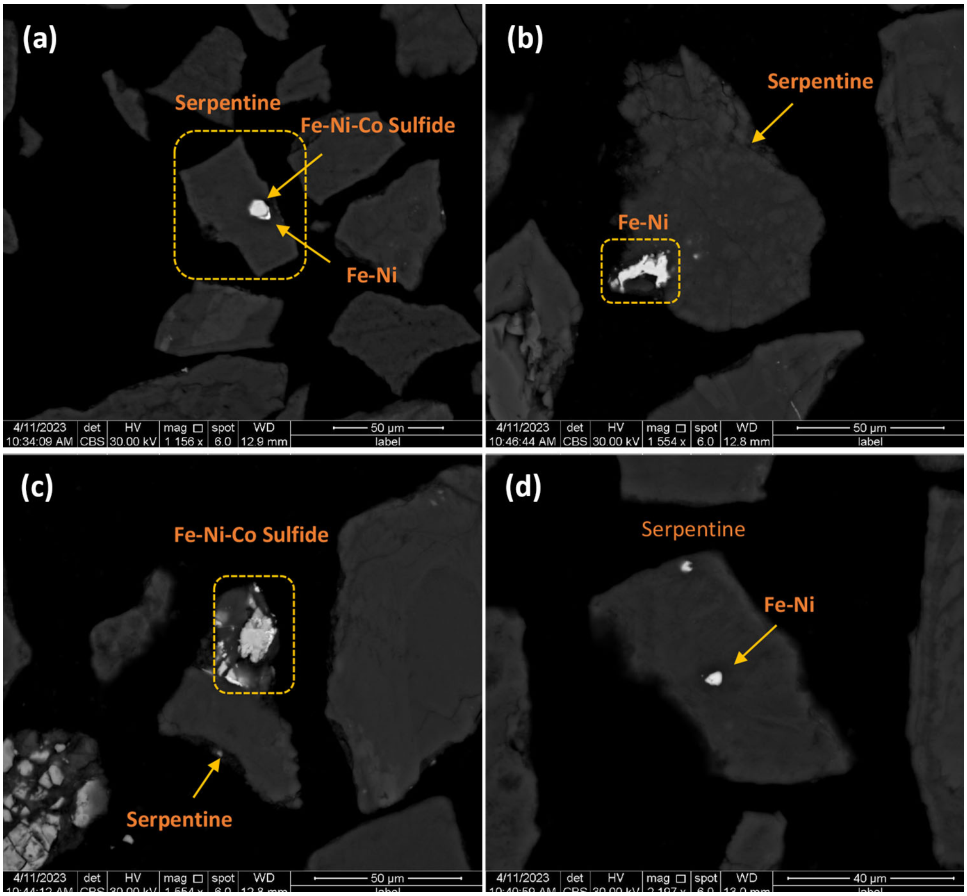

Fig. 3. Backscattered electron images and mineral liberation analysis classified images: (a) Fe-Ni-Co sulfide and Fe-Ni, (b) Fe-Ni, (c) Fe-Ni-Co sulfide and (d) Fe-Ni minerals locked in serpentine.

Table II. Presence of Ni-bearing mineral in the tailings

	Particle size (*µ*m)		
Ni-bearing mineral	**− 106 + 75**	**− 75 + 50**	**− 50 + 38**
Fe-Ni	90.71% serpentine 3.27% pyroxene 3.22% olivine	86.11% serpentine 1.74% clinochlore 2.66% Fe-Ni-Co_sulfide	86.07% serpentine 8% Fe-Ni-Co sulfide
Fe-Ni-Co sulfide	71.73% serpentine 28.27% olivine	88.58% serpentine 9.51% Fe-Ni	79.71% serpentine 11.67% Fe-Ni

solid ratio) resulted in an increase in the leaching rate of Ni from the tailings. These findings were in good agreement with those of previous studies,[39,40] which suggested conducting leaching tests at a lower solid ratio to obtain a high Ni extraction rate in H_2SO_4 solution. However, other parameters, acid concentration (1, 3 and 7) and time (0.5, 1 and 2), were different. It was thought that solid-to-liquid ratio played a key role during leaching, but the effects of other parameters on the leaching behavior of Ni were not satisfactory in this study, which is not consistent with the findings of previous studies conducted on laterite ores. These thoughts are in good agreement with the S/N results. It was aimed to obtain a high Ni extraction rate from the sample and therefore the "larger is better" was selected to evaluate the experimental results by analyzing the S/N ratio. It is clearly seen that the most important parameter for the Ni extraction rate was solid-to-liquid ratio, whereas no remarkable effects were observed with any changes in the other leaching parameters. A decrease in the solid-to-liquid ratio resulted in an increase in the extraction rate of Ni from the tailings. However, the effects of other

Table III. Mineral associations for Fe-Ni and Fe-Ni-Co sulfide minerals in the tailings (binary: two phases detected, ternary + particle: as least three mineral phases detected)

Fe-Ni particle size (− 106 + 75 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	91.69	5.73
Pyroxene	0.00	0.44
Olivine	1.95	0.00
Fe-Ni particle size (− 75 + 50 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	90.20	5.30
Clinochlore	0.00	1.51
Olivine	2.75	0.00
Fe-Ni-Co sulfide	0.00	0.25
Fe-Ni Particle size (− 50 + 38 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	71.92	18.57
Fe-oxide	0.00	1.81
Pyroxene	0.00	7.71
Fe-Ni-Co sulfide Particle size (− 106 + 75 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	1.82	92.35
Pyroxene	0.00	0.47
Olivine	0.00	5.35
Fe-Ni-Co sulfide Particle size (− 75 + 50 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	100.00	0.00
Fe-Ni-Co sulfide Particle size (− 50 + 38 μm)	Binary particle (%)	Ternary + particle (%)
Serpentine	100.00	0.00

Table IV. Experimental results obtained in physical separation tests

Products	Cr_2O_3 (%)	Ni (ppm)	% weight	% Cr_2O_3 recovery	% Ni recovery
Test: magnetic separation					
Feeding material	3.53	200	100		
Magnetic product	21.12	196	12.66	75.75	12.41
Non-magnetic product	0.98	203	87.34	24.25	88.65
Test: falcon concentrator					
Feeding material (magnetic product)	21.12	196	100		
Heavy product (concentrate)	37.45	198	38.65	68.53	69.23
Light product (tailings)	10.83	197	61.35	31.46	31.62

parameters on the extraction rate of Ni were negligible, as can be seen in S/N graphs given in Fig. 4.

The highest leaching efficiency of Ni was found to be 98.8% by conducting the following leaching conditions (experiment no. 6): acid concentration of 3 M, reaction time of 2 h and solid-to-liquid ratio of 1:20 at ambient temperature (25°C). The pH of the PLS was around 0. However, the Cr extraction rate was higher (4.7%) compared with the other leaching tests. Furthermore, the extraction rates of other elements (Fe, Mg, Ca and Al) classified as impurities were lower than that of 10%. Finally, the pregnant leach solution (PLS) contained 99 mg/L Ni, 8 mg/L Cr, 640 mg/L Fe, 404 mg/L Mg and 95 mg/L Ca. Surianti et al.[41] suggested that the precipitation of Ni as oxalate form should be investigated at higher temperatures (90°C) making the precipitation rate of Ni high. Therefore, 250 mL PLS was mixed with the same volume of 1 M oxalic acid and stirred at 300 rpm for 3 h at a temperature of 90°C. Ni concentration before and after the mixing of PLS and oxalic acid solution was measured by AAS and ICP-OES. Allen[42] examined the mechanism of the precipitation behavior of Ni as nickel oxalate and suggested the following equations (Eqs. 8 and 9), which represent the chemical reaction between Ni ions and oxalic acid during the

Table V. Experimental results obtained in this study

Experiment no.	Ni extraction (%)	Cr extraction (%)
No. 1	6.55	0.21
No. 2	19.52	0.66
No. 3	53.94	2.57
No. 4	91.78	3.01
No. 5	49.01	1.96
No. 6	98.88	4.76
No. 7	15.30	0.07
No. 8	26.93	0.97
No. 9	86.23	3.77
No. 10	83.71	3.97
No. 11	22.88	0.69
No. 12	7.28	0.16
No. 13	24.54	0.95
No. 14	6.82	0.16
No. 15	97.90	5.38
No. 16	63.04	3.22

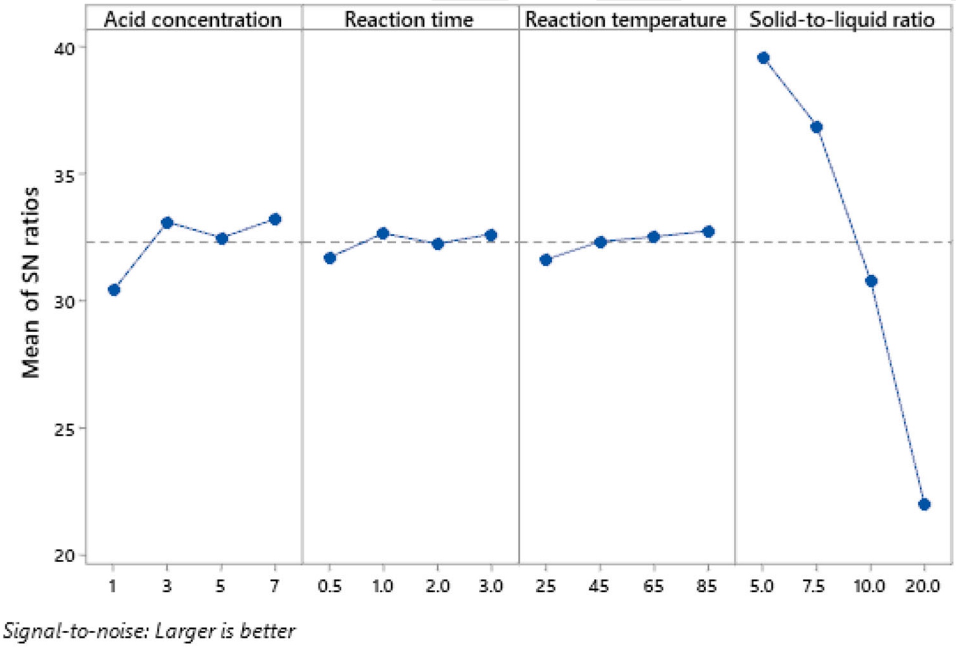

Fig. 4. Influence of leaching conditions on the Ni extraction rate from the sample [points of solid-to-liquid ratio of 5 → 1:20, 7.5 → 1:15, 10 → 1:10, 20 → 1:5].

precipitation. It was determined that Ni was precipitated as the form of nickel oxalate dehydrate with a precipitation rate of 72%.

$$2NiSO_{4(aq)} + 2H_2C_2O_{4(aq)} \leftrightarrow [Ni(C_2O_4)_2]^{-}Ni^{++}_{(aq)} + 2H_2SO_{4(aq)} \quad (8)$$

$$[Ni(C_2O_4)_2]^{-}Ni^{++}_{(aq)} \rightarrow 2NiC_2O_4 \cdot 2H_2O_{(s)} \quad (9)$$

CONCLUSION

In this study, the recovery of Ni from the tailings obtained from chromite beneficiation plants was investigated. Before the beneficiation process, mineral liberation analysis was carried out to identify the properties of the tailings used in this study. Ni phases in the tailings determined by mineral liberation analysis were as follows: Fe-Ni and Fe-Ni-Co sulfide minerals. These minerals are hosted in serpentine, pyroxene, clinochlore and olivine minerals. Liberated fine chromite minerals are recovered using the magnetic separation process followed by Falcon concentrator. The chromite product with a Cr_2O_3 grade 37.45% was obtained. The leaching behavior of Ni was investigated at different conditions (acid concentration, temperature, time and solid-to-liquid ratio) based on the Taguchi approach, which indicates that the solid-to-liquid ratio played a key role in the leaching, whereas other parameters had no strong effects. Ni with an extraction rate of $> 98\%$ was successfully dissolved in H_2SO_4 solution (3 M) with a solid-to-liquid ratio of 1:20 at ambient temperature for 2 h. Finally, Ni was precipitated from the PLS via oxalate precipitation. Considering all experimental results, the tailings may be a good alternative source for Ni demand in the future.

SUPPLEMENTARY INFORMATION

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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